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Scientific paper

Kinetics and Mechanism of the Ligand Exchange Reaction Between Tetraaza Macrocycle Ligand and Cu(II) Tetradentate Amine-Amide Complexes

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Abstract

The kinetics of the ligand exchange reaction of tetraaza macrocycle, teazma (teazma is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydrogen perchlorate) with $Cu(bcen)^{2+}$ and $Cu(bctn)^{2+}$, where bcen and bctn are *N,N*'-bis(β-carbamoylethyl) ethylendiamine) and *N,N*'-bis(β-carbamoylethyl) propylendiamine), respectively, have been studied by visible spectrophotometry in dimethylformamide, DMF, solvent at 25 ± 0.2 °C. In the system of $Cu(bctn)^{2+}$/teazma, the ligand exchange reaction proceeds in a two-step-consecutive manner, with two rate constants $k_{obsd}^{bctn}(1)$ and $k_{obsd}^{bctn}(2)$. The first reaction step was dependent on the concentration of teazma macrocycle, while the second reaction step was independent. However, it is found that the ligand exchange reaction in $Cu(bcen)^{2+}$/teazma proceeds in an one-step with the rate constant k_{obsd}^{bcen}. The rate constant is dependent on [teazma] macrocycle. The ligand exchange reaction in the system of $Cu(bcen)^{2+}$/teazma is not complete and after some progress, the reaction reaches equilibrium. On the basis of results, a reaction mechanism is proposed and discussed for the ligand exchange rate.

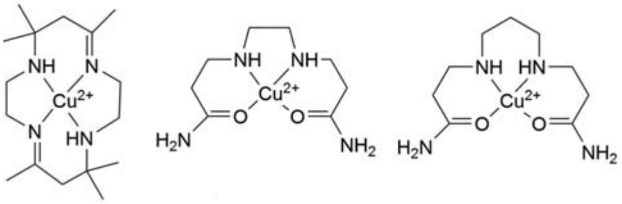
Keyword: Macrocycle, acyclic, diamine diamide, Cu complexes, ligand exchange

1. Introduction

Complexes with chelating ligands generally have increased stability relative to those of monodentate ligands, and even greater stability when the donor atoms are incorporated into a cyclic ligand that surrounds the metal ion, commonly referred to as a »macrocyclic effect«.[1–3] The chemistry of transition metal ion with macrocyclic ligands is an interesting field in chemistry and has been the subject of extensive research due to their potential applications in different fields, such as coordination chemistry, environmental chemistry and the role they play as models for metalloproteinase and enzymes binding sites in biological systems.[3–11]

Macrocyclic ligands represent an interesting class of ligands in compared with acyclic multidentate ligands. Macrocyclic complexes show thermodynamic and kinetic stabilities and the characteristic properties inaccessible to the complexes of non-cyclic chelate ligands. Cyclic tetraaza are among the most intensively studied macrocyclic ligands forming stable and inert complexes with many transition metal ions.[9–15] Tetraaza macrocycles are coordinated by four donor atoms N to central ion, usually the central ion is coplanar with the four nitrogen atoms.[3,8,16]

Our group has studied the ligand exchange of copper(II) and nickel(II) complexes by acyclic tetradentate ligands.[17–19] As an extension of our study, we have been interested in the possibility of ligand exchange reaction between $Cu(bcen)^{2+}$ and $Cu(bctn)^{2+}$, where bcen and bctn are acyclic diamine-diamide tetradentate ligand, *N,N*'-bis(β-carbamoylethyl) ethylendiamine) and *N,N*'-bis(β-carbamoylethyl) propylendiamine), respectively, with tetraaza



$Cu(teazma)^{2+}$ $Cu(bcen)^{2+}$ $Cu(bctn)^{2+}$

Scheme 1. A structural representation of copper complexes.

macrocycles, teazma (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo tetradeca-4,11-diene dihydrogen perchlorate, Scheme 1) in order to gain better understanding of the kinetic and mechanistic behavior of multidentate ligand exchange processes.

2. Experimental

2. 1. Reagents

The acyclic diamine-diamide tetradentate ligand, bcen, bctn, and copper complexes were prepared as previously reported elsewhere by us and others.[20,21]

The macrocycle ligand teazma was prepared by the reported method.[22] The reaction of perchloric acid with ethylenediamine (1:1 molar ratio) in acetone solvent at room temperature for 15 min to give a white precipitate. m.p. >110 °C, Yield 70%. Anal. Calcd for $C_{16}H_{34}Cl_2N_4O_8$: C, 39.92, H, 7.12; N, 11.64. Found: C, 40.15; H, 7.19; N, 11.73. IR (KBr, cm^{-1}): υNH = 3147, υC=N = 1667, υCN = 1175, υClO_4 = 1052.

The macrocycle complex $[Cu(teazma)](ClO_4)_2$ was prepared as previously reported.[23] Yield 82%. Anal. Calcd for $C_{16}H_{32}Cl_2CuN_4O_8$: C, 35.40, H, 5.94; N, 10.32. Found: C, 35.35; H, 6.02; N, 10.23. IR (KBr, cm^{-1}): υNH = 3212, υC=N = 1672, υCN = 1175, υClO_4 = 1037.

All other chemicals and solvent used in this work were of analytical grade, available commercially and were used without further purification.

2. 2. Kinetic Measurements

The kinetic ligand exchanges of Cu(II) complexes, $Cu(bcen)^{2+}$ and $Cu(bctn)^{2+}$, were studied under pseudo first order conditions with an excess amount of [teazma] in dimethylformamide, DMF, as solvent. The concentration of Cu(II) complexes were kept constant at 6.50×10^{-3} M, while [teazma] was varied from 6.50×10^{-3} to 1.63×10^{-1} M. All reactions were performed at 25 ± 0.2 °C and $NaClO_4$ were used to maintain a constant ionic strength of 1.0 M. The equal volumes (1 mL) of the isothermal reacting stock solutions of macrocycle ligand and $NaClO_4$ and copper complex were taken by a syringe and mixed in cell (1 cm path length). The ligand exchange reactions were monitored by a GBC UV-Visible Cintra 101 spectrophotometer and following the increase in absorbance at 515 nm due to the formation of $Cu(teazma)^{2+}$ complex. The wavelength 515 nm is the maximum absorption of $Cu(teazma)^{2+}$ complex (see Fig. 1). Each run was studied at least three times.

The absorbance versus time data were computer fitted by sigmaplot 12.0 software with equations 1 (monophasic reaction) and 2 (biphasic reaction) to find the best fit and k_{obs}.[24,25]

$$A = a_1\exp[-k_{obsd}(1)t] + A_\infty \qquad (1)$$

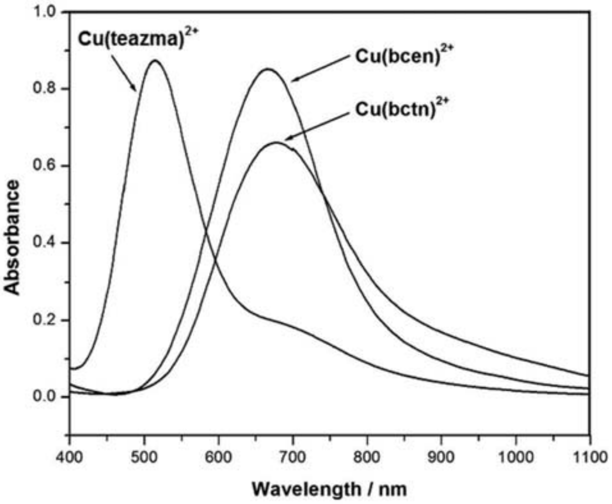


Fig.1. Visible spectra of $Cu[(teazma)](ClO_4)_2$, $Cu(bcen)(NO_3)_2$ and $Cu(bctn)(NO_3)_2$, (6.5×10^{-3} M) complexes in DMF (1 cm quartz cell).

$$A = a_1\exp[-k_{obsd}(1)t] + a_2\exp[-k_{obsd}(2)t] + A_\infty \qquad (2)$$

where a_1 and a_2 are comprised of rate constants and molar absorptivities.

3. Results and Discussion

3. 1. Proposed Mechanism of $Cu(bctn)^{2+}$/teazma System

The spectral changes associated with ligand exchange in $Cu(bctn)^{2+}$ by teazma according to eq. 3 are shown in Fig. 2. The presence of only two absorbing species in the reaction mixture during the reaction course is confirmed by a sharp single isosbestic points at ca. 600 nm. The

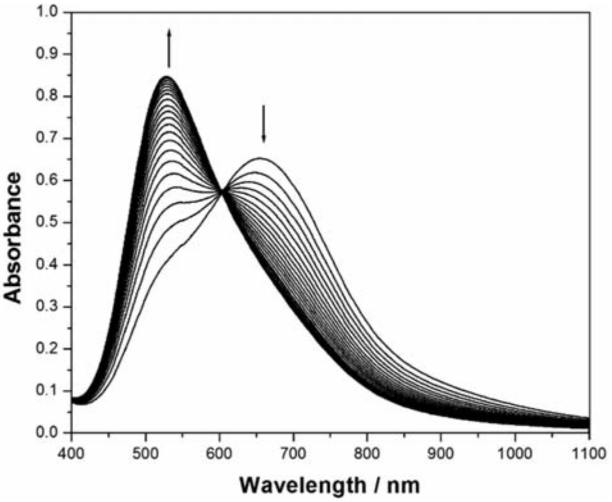


Fig. 2. Spectral changes recorded in DMF solvent for the reaction of $Cu(bctn)(NO_3)_2$, (6.50×10^{-3} M)/ teazma (6.50×10^{-3} M) system.

change proceeds with a decrease in absorbance at ca. 675 nm and an increase at ca. 515 nm. The absorbance at 515 nm 675 nm due to Cu(teazma)$^{2+}$ and Cu(bctn)$^{2+}$ complexes, respectively (see Fig. 1).

$$\text{Cu(bctn)}^{2+} + \text{teazma} \rightarrow \text{Cu(teazma)}^{2+} + \text{bctn} \qquad (3)$$

The kinetics of ligand exchange were followed by monitoring the increase in absorbance at 515 nm, the wavelength of maximum absorption due to the formation of Cu(teazma)$^{2+}$ complex (Fig. 2). An example plot of absorbance versus time is shown in Fig. 3. The plot exhibited a monotonic increase and the pseudo-first-order rate constants (k_{osed}) were calculated from the absorbance changes at this wavelength.

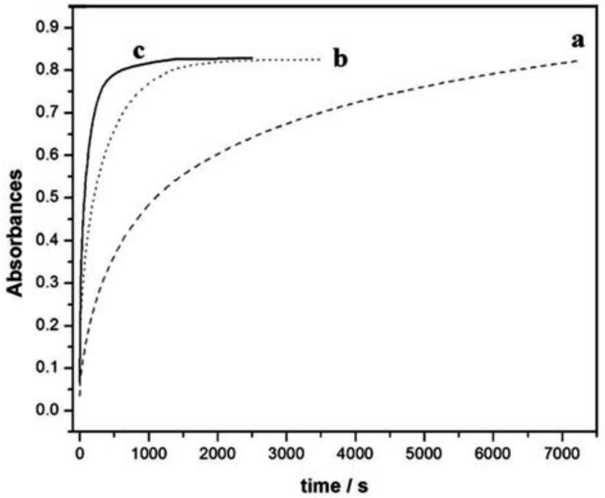


Fig. 3. Plot of absorbance vs. time for reaction of Cu(bctn)(NO$_3$)$_2$, (6.50 × 10^{-3} M) and teazma, **a** = 6.50 × 10^{-3} M, **b** = 6.50 × 10^{-2} M, **c** = 1.63 × 10^{-1} M recorded in DMF solvent.

The rate constants, k_{osed} were calculated by fitting the kinetic curves, absorbance vs. time with the help of a suitable exponential computer-fit program. The best fit was obtained by equation 2 (biphasic reaction) for Cu(bctn)$^{2+}$/teazma system. Therefore, the kinetics Cu(bctn)$^{2+}$/teazma system are taking place in two consecutive steps, i.e. the ligand exchange reaction proceeds in a two-step-consecutive manner (A → B → C), with two the rate constants $k^{bctn}_{obsd}(1)$ and $k^{bctn}_{obsd}(2)$. Table 1 summarizes values of k_{obsd} for various concentration of teazma macrocycle.

The rate constants of the two consecutive steps are first order for Cu(bctn)$^{2+}$ complex. The effect of the teazma concentration on the experimental rate constants, $k^{bcnt}_{obsd}(1)$ and $k^{bctn}_{obsd}(2)$ is shown in Fig. 4. The rate constant of the first-step, $k^{bctn}_{obsd}(1)$ increases linearly with increasing [teazma]. Based on this, the first step is first order in [Cu(bctn)$^{2+}$] and [teazma]. The rate constant of the second-step, $k^{botn}_{obsd}(2)$ found to be independent on the concentration of teazma macrocycle. The small intercept confirms that the reverse reaction does not take place and also the negligible contribution of solvent to the overall rate.[24,26,27] Therefore, the rate law applicable to kinetic ligand exchange Cu(bctn)$^{2+}$/teazma system is given by eq. 4.

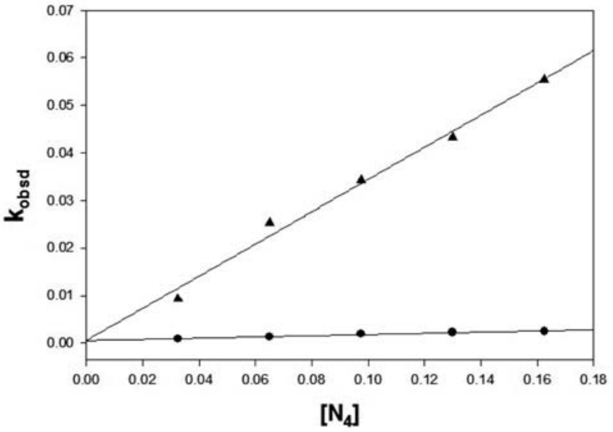


Fig.4. Plot of the rate constants $k^{bctn}_{obsd}(1)$ ▲ and $k^{bctn}_{obsd}(2)$, ● vs. teazma for Cu(bctn)(NO$_3$)$_2$, (6.50 × 10^{-3} M) complex .

$$\text{Rate} = k^{bctn}_{obsd}[(1) + k^{bctn}_{obsd}(2)][\text{Cu(bctn)}^{2+}] \qquad (4)$$

Where

$$k^{botn}_{obsd}(1) = k^{bctn}(1)[\text{teazma}] \qquad (5)$$

$$k^{botn}_{obsd}(2) = k^{bctn}(2) \qquad (6)$$

The $k^{bctn}(1)$ value was obtained from the slop of the linear plot $k^{bctn}_{obsd}(1)$ vs. [teazma] (eq. 5) and $k^{bctn}(2)$ which was independent on concentration teazma, was computed from the average of the values obtained for $k^{bctn}_{obsd}(2)$, (Fig. 4 and Table 1). The rate constant for the second-step $k^{bctn}(2) = 3.44 \pm 0.11 \times 10^{-3}$ s^{-1}) is ca. 100 times slo-

Table 1. Rate constants data for the reaction of Cu complexes, 6.5 × 10^{-3} M, with teazma ligand in DMF

complex		**10^2 × [teazma] / M**					
		3.25	**6.50**	**9.75**	**13.0**	**16.3**	***k***
Cu(bctn)$^{2+}$	$10^2 \times k^{bctn}_{obsd}(1)$ / s^{-1}	1.10 ± 0.12	2.70 ± 0.15	3.60 ± 0.29	4.50 ± 0.22	5.70 ± 0.24	$10^1 \times k_1 = 3.39 \pm 0.22$ / M^{-1} · s^{-1}
	$10^3 \times k^{bctn}_{obsd}(2)$ / s^{-1}	2.96 ± 0.15	3.15 ± 0.19	3.42 ± 0.17	3.83 ± 0.12	3.85 ± 0.10	$10^3 \times k_2 = 3.44 \pm 0.15$ / s^{-1}
Cu(bcen)$^{2+}$	$10^4 \times k^{bcen}_{obsd}$ / s^{-1}	5.40 ± 0.15	6.21 ± 0.22	7.48 ± 0.11	9.02 ± 0.41	10.3 ± 0.68	$10^3 \times k_1 = 3.78 \pm 0.23$ / M^{-1} · s^{-1} $10^4 \times k_{-1} = 3.99 \pm 0.25$ / s^{-1}

wer than that of first-step $k^{botn}(1) = 3.39 \pm 0.22 \times 10^{-1}$ $M^{-1} \cdot s^{-1}$).

A mechanism of two step as shown in scheme 2 has been suggested for the reaction of Cu(bctn)$^{2+}$ complex with teazma macrocycle. The first step is assigned to the reaction between Cu(bctn)$^{2+}$ complex and teazma ligand to give Cu(bctn)$^{2+}$·teazma intermediate. The intermediate can be a species with both bctn and macrocycle ligands are partially coordinated to the copper. The suppose of the formation of the adduct Cu(bctn)$^{2+}$·teazma is according to studies on ligand exchange reaction between polydentate. The incoming ligand is partially coordinated to the metal center and the leaving ligand is partially dissociated.[18,19,28–30]

The second step of reaction is the first-order and independent on [teazma] macrocycle with rate constant $k^{bctn}(2)$. The rate of the ligand exchange reaction is controlled by this step (rate-determining step). This step of reaction is the stepwise breakage of the second copper-nitrogen bond by the stepwise coordination the nitrogen of teazma macrocycle. The suggested mechanism is in according with mechanism of the dissociation reaction Cu(bctn)$^{2+}$ reported by Chung which the rate-determining step is the rupturing of the second copper(II)-nitrogen bond.[21]

3. 2. Proposed Mechanism of Cu(bcen)$^{2+}$/teazma System

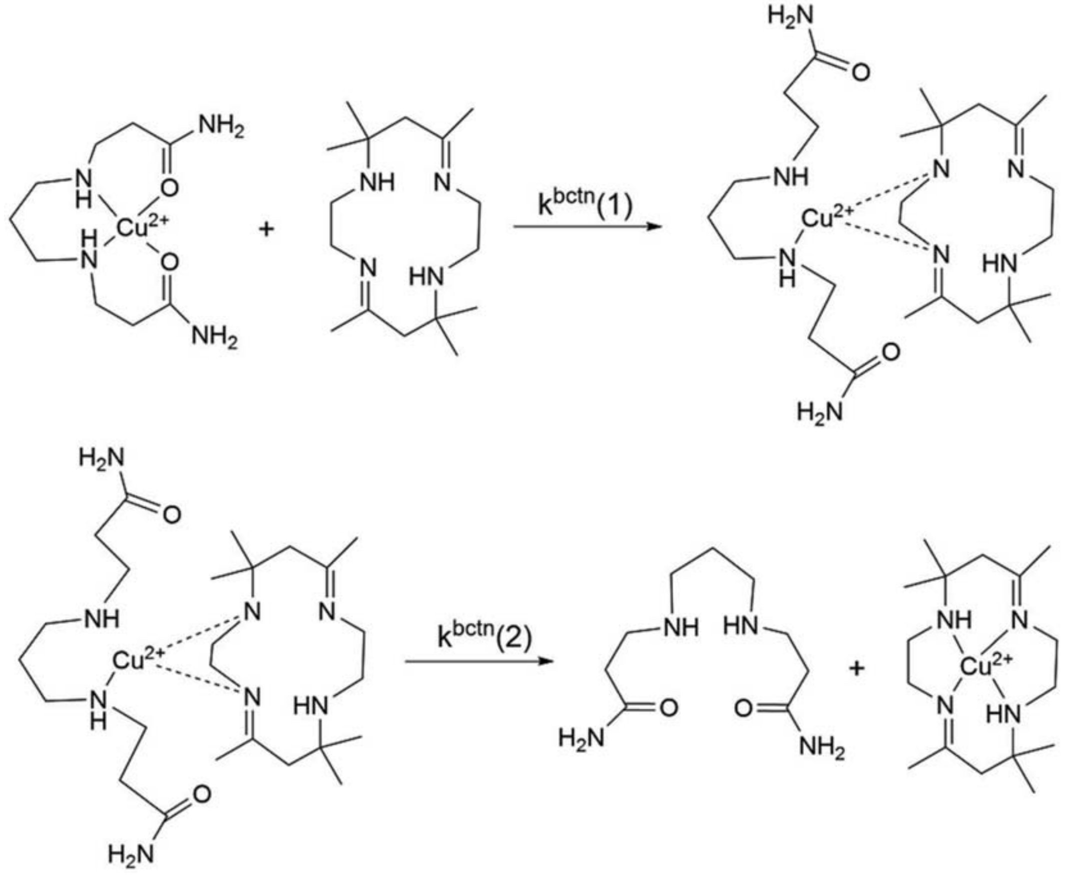
The rate constants for ligand exchange reaction of Cu(bctn)$^{2+}$ complex by teazma were obtained by measuring the absorbance changes at 515 nm under the pseudo-first-order. The absorbance at 515 nm was found to increase with elapse of time (Fig. 5).

Under these conditions, the best fit of the absorbance versus time data were obtained by Equation 1 (monophasic reaction). Therefore, the rate constant k_{obsd}^{bcen} in Cu(bcen)$^{2+}$/teazma system was obtained. The pseudo-first-order rate constant k_{obsd}^{bcen} was found to increase with increase in teazma concentration (Fig. 6), the k_{obsd}^{bcen} values are collected in Table 1.

Fig. 7 shows a consecutive series of spectra recorded in DMF solvent for the Cu(bcen)$^{2+}$/teazma system. Comparing Figure 7 with Figures 1 and 5 shows that the ligand exchange reaction is not complete and after some progress, the reaction reaches equilibrium (Eq. 7).

$$\mathrm{Cu(bcen)^{2+} + teazma \rightleftharpoons Cu(teazma)^{2+} + bcen} \qquad (7)$$

The effect of the teazma concentration on the rate constants, k_{obsd}^{bcen} is shown in Fig. 6. The rate constant in-



Scheme 2. The suggest mechanism for ligand exchange reaction in the system Cu(bctn)(NO$_3$)$_2$/teazma system.

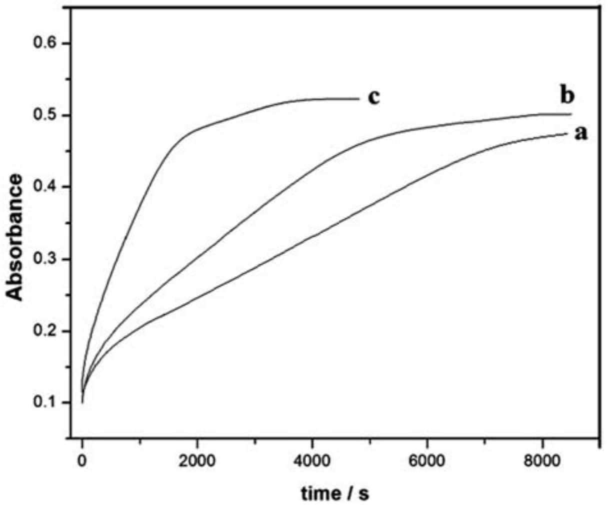


Fig. 5. Plot of absorbance vs. time for reaction of Cu(bcen)(NO_3)$_2$, (6.50 × 10^{-3} M) and teazma, **a** = 6.50 × 10^{-3} M, **b** = 9.8 × 10^{-2} M, **c** = 1.63 × 10^{-1} M recorded in DMF solvent.

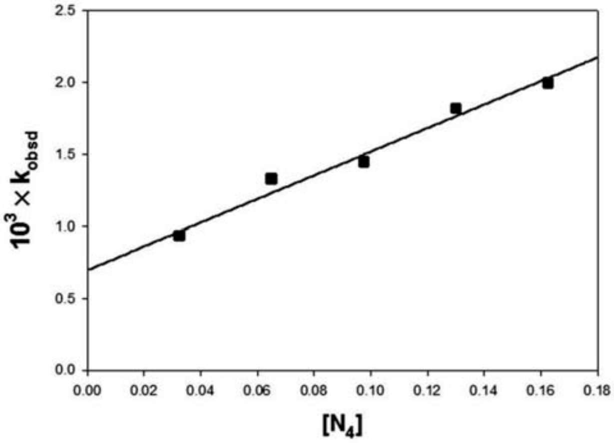


Fig. 6. Plot of the rate constant k_{obsd}^{botn} vs. teazma for Cu(bcen)(NO_3)$_2$, (6.50 × 10^{-3} M) complex .

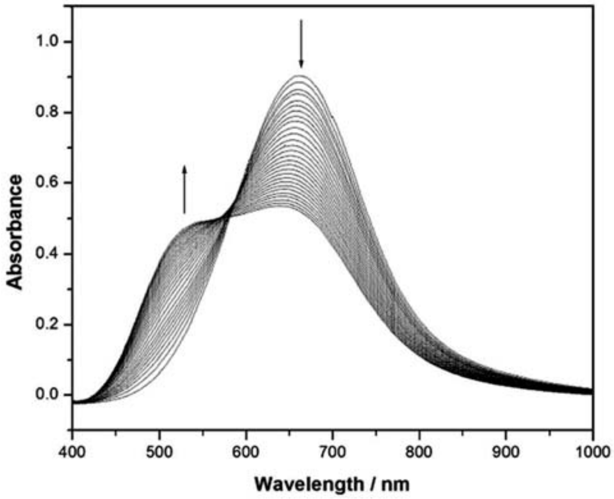


Fig. 7. Spectral changes recorded in DMF solvent for the reaction of Cu(bcen)(NO_3)$_2$, (6.50 × 10^{-3} M)/ teazma (6.50 × 10^{-3} M) system.

creases linearly with increasing [teazma]. Likewise, as shown in Fig. 6, the dependence of rate constant k_{obsd}^{bcen} on the excess concentration of teazma is linear with non-zero intercepts confirms that the reverse reaction does take place. The rate law can be expressed by Eq. 8.

$$\text{Rate} = k_{obsd}^{bcen}[\text{Cu(bcen)}^{2+}] = (k_1^{bcen}[\text{teazma}] + k_{-1}^{bcen})\,[\text{Cu(bcen)}^{2+}] \qquad (8)$$

The rate constants k_1^{bcen} value was calculated according to the Eq. 8 from the slope k_{obsd}^{bcen} vs. [teazma], whereas the value for the reverse rate constant (k_{-1}^{bcen}) was obtained from the intercept the plot (Table 1). The value k_{-1}^{bcen} = 3.99 × 10^{-4} s^{-1}, is close to the rate constant of dissociation for Cu(bcen)$^{2+}$ (k_{diss} = 8.81 × 10^{-5} s^{-1}).[21]

Chung reported the values of the rate constants of dissociation for Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$ in water 7.94 × 10^{-3} and 8.81 × 10^{-5} s^{-1}, respectively.[21] The ratio of the rate constants for the ligand exchange of the Cu(bctn)$^{2+}$/teazma and Cu(bcen)$^{2+}$/teazma systems (k_1^{bctn}/k_1^{bcen} = 89.7) are compatible with the ratio of the rate constants of dissociation reported by Chung for Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$ (90.1).[21] Comparisons of the ratios of the rate constants obtained in this study and the rate constants of dissociation for Cu(bten)$^{2+}$ and Cu(bcen)$^{2+}$, show that the two reactions (ligand exchange and dissociation reactions) have the same the rate determining step. The rate-determining step for dissociation Cu(bctn)$^{2+}$ and Cu(bcen)$^{2+}$ are the breakage of second copper nitrogen bond.[21] The similarly of the values of k_{-1}^{bcen} and the rate constants of dissociation of Cu(bcen)$^{2+}$ can be the reason for the ligand exchange reaction was not complete and after some progress the forward reaction the reverse reaction is performed.

4. Conclusion

The ligand exchange reaction was investigated by using visible spectrophotometry in the dimethylformamide, DMF, as solvent. In the system Cu(bctn)$^{2+}$/teazma, the ligand exchange reaction proceeds in a two-step-consecutive manner, with two the rate constants (1) and (2), and the ligand exchange reaction was completed. The rate-determining step is the breaking of the second copper(II)-nitrogen bond. The ligand exchange reaction in the system Cu(bcen)$^{2+}$/teazma is not complete and is reversible reaction. The same value of the reverse rate constant in the system with the rate constant of dissociation of Cu(bcen)$^{2+}$ complex, can be the reason for the reversibility of the reaction.

5. Acknowledgements

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Povzetek

S pomočjo spektrofotometrije smo v dimetilformamidu (DMF) kot topili pri 25 ± 0.2 °C spremljali kinetiko izmenjave tetraaza makrocikličnega liganda teazma (teazma je 5,7,7,12,14,14-heksametil-1,4,8,11-tetraazaciklotetradeka-4,11-dien dihidroperklorat) z Cu(bcen)$^{2+}$ in Cu(bctn)$^{2+}$, kjer sta bcen in bctn *N*,*N*'-bis(β-karbamoiletil) etilendiamin in *N*,*N*'-bis(β-karbamoiletil) propilendiamin. V sistemu Cu(bctn)$^{2+}$/teazma, poteka izmenjava liganda v dvostopenjskem zaporedju, z dvema hitrostnima konstantama (1) in (2). Prvi reakcijski korak je odvisen od koncentracije makrocikličnega liganda teazma, medtem ko je drugi reakcijski korak neodvisen. Izmenjava ligandov pri sistemu Cu(bcen)$^{2+}$/teazma poteka v eni stopnji s hitrostno konstanto . Hitrostna konstanta je odvisna od koncentracije teazma makrocikličnega liganda. Izmenjava ligandov v sistemu Cu(bcen)$^{2+}$/teazma ne poteče do konca, ampak se po določenem času vzpostavi ravnotežje. Na podlagi dobljenih rezultatov je predlagan reakcijski mehanizem in obravnavana hitrost izmenjave ligandov.